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(11) Publication number:

0 663 460 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94300252.7**(51) Int. Cl.⁶: **C25D 3/60**(22) Date of filing: **13.01.94**(43) Date of publication of application:
19.07.95 Bulletin 95/29(84) Designated Contracting States:
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London EC4A 1PQ (GB)(54) **Tin-zinc alloy electroplating bath and method for electroplating using the same.**

(57) A tin-zinc alloy electroplating bath comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water. When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case where the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substance having a complicated shape and the chromate treatment becomes satisfactory. As a result, the effect of the coating is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

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The present invention relates to a tin-zinc alloy electroplating bath and a method for electroplating using the same. In particular, the present invention relates to a tin-zinc alloy electroplating bath capable of stably forming a coating of a uniform alloy composition by keeping the plating alloy composition from the influence of the current density.

The tin-zinc alloy electroplating method attracted attention, and recently has come to be widely used as an industrial plating method for automobile parts and electronic parts, since the electroplated products have excellent corrosion resistance, aqueous salt solution resistance and solderability.

The plating baths heretofore proposed for the tin-zinc alloy electroplating include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, sulfonate bath, carboxylate bath and cyanide-free alkaline bath. Some of them are practically used.

A defect common to the conventional tin-zinc alloy plating baths is that the current density exerts a strong influence on the composition of the plating alloy. Namely, even when the current density during the plating is fixed, the current density distribution on the surface of the substance to be plated is not always even and, therefore, the composition of the plating alloy is ununiform. This phenomenon is marked particularly when the substance has a large surface to be plated or a complicated shape.

As a result, the properties of the coating and the quality of the plated substance, i.e. the corrosion resistance, chromate coating film-forming properties and solderability, become various.

As an electroplating bath having small influence due to change in current density, Japanese Patent Publication for Opposition Purpose (hereinafter referred to as "J.P. KOKOKU") No. Sho 57-2795 proposes a citrate bath containing a water-soluble brightener obtained by reacting phthalic anhydride with a reaction product of an aliphatic amine and an organic acid ester, and the bath is now practically used. J.P. KOKOKU No. Sho 57-2796 also discloses a tin-zinc alloy plating bath containing specified amounts of tin sulfate and zinc sulfate and further citric acid (or its salt), ammonium sulfate and sodium sulfate. Further, J.P. KOKOKU No. Sho 59-48874 discloses a tin-zinc alloy plating bath containing citric acid (or its salt), an ammonium salt and a specified polymer.

However, even when such a bath is used for the electroplating, the uniformity of the alloy composition is insufficient, since the plating alloy composition on certain part of surface of substrate having an extremely low current density has a high tin content. Under these circumstances, special facilities are necessitated and a strict operation control is indispensable at present.

A primary object of the present invention is to provide an electroplating bath capable of forming a coating film having a high quality and comprising a homogeneous tin-zinc plating alloy composition at a current density in a wide range.

Another object of the present invention is to provide a method for forming a homogeneous tin-zinc plating alloy composition on a substrate by electroplating in a tin-zinc electroplating bath.

These and other objects of the present invention will be apparent from the following description and examples.

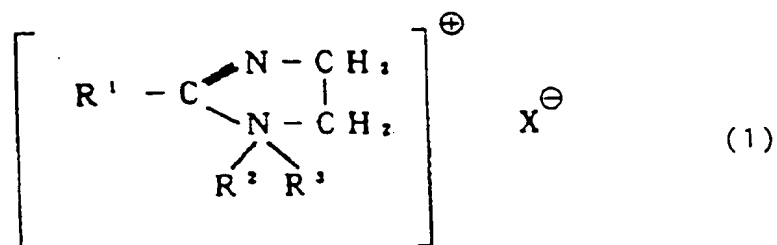
The present invention was completed on the basis of a finding that the above-described problem can be efficiently solved by adding an amphoteric surfactant to a tin-zinc plating bath.

Namely, the present invention provides a tin-zinc alloy electroplating bath which comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water.

The present invention further provides a method for forming a tin-zinc plating alloy on a substrate by electroplating in the above-mentioned tin-zinc electroplating bath wherein the substrate is a cathode and tin-zinc alloy is an anode.

Although the amount of the amphoteric surfactant contained in the tin-zinc alloy electroplating bath is not particularly limited in the present invention, it is preferably 0.01 to 30 g/l, more preferably 0.3 to 15 g/l. When it is below 0.01 g/l, the effect is insufficient and, on the contrary, when it exceeds 30 g/l, the bath is foamed during the plating and the current efficiency is lowered.

The amphoteric surfactants usable herein include those of, for example, imidazoline, betaine, alanine, glycine and amide types. Among them, preferred amphoteric surfactants of imidazoline type are those having a structure of the following formula (1):



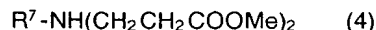
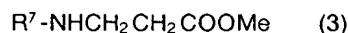
wherein X represents a halogen, hydroxyl group, sulfuric acid group or hydroxyalkanesulfonic acid group or hydroxycarboxylic acid group having 1 to 10 carbon atoms, R¹ represents an alkyl group having 8 to 20 carbon atoms, R² represents an alkyl group having 1 to 5 carbon atoms and containing a hydroxyl group, and R³ represents a carboxylic acid or sulfonic acid having 1 to 10 carbon atoms or its salt or sulfuric acid ester salt.

The amphoteric surfactants of betaine type are preferably those having a structure of the following formula (2):



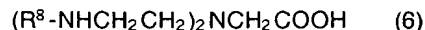
wherein R⁴ represents an alkyl group having 8 to 20 carbon atoms, and R⁵ and R⁶ may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms, Me represents an alkali metal (same in the below),

The amphoteric surfactants of alanine type are preferably those having a structure of the following formula (3) or (4):



wherein R⁷ represents an alkyl group having 8 to 20 carbon atoms.

The amphoteric surfactants of glycine type are preferably those having a structure of the following formula (5) or (6):



wherein R⁸ represents an alkyl group having 8 to 20 carbon atoms. The amphoteric surfactants of amide type are preferably those having a structure of the following formula (7):



wherein R⁹ represents an alkyl group having 8 to 20 carbon atoms.

These amphoteric surfactants can be used either singly or in combination of two or more of them.

The tin-zinc alloy electroplating baths of the present invention include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, silicofluoride bath, sulfonate bath, carboxylate bath, cyanide-free alkaline bath, gluconate bath and organic acid bath. The bath contains a water soluble stannous salt such as stannous sulfate in an amount of usually 1 to 100 g/l (in terms of metallic tin), preferably 5 to 50 g/l, and a water soluble zinc salt such as zinc sulfate in an amount of usually 0.2 to 80 g/l (in terms of metallic zinc), preferably 25 to 40 g/l. Particularly preferred is the cyanide-free bath. The bath can contain 40 to 400 g/l of a carboxylic acid having 1 to 15 carbon atoms, preferable 3 to 7 carbon atoms such as citric acid or

gluconic acid, 30 to 300 g/l of pyrophosphoric acid or 40 to 400 g/l of sulfamic acid. The pH of the bath ranges from 3 to 10.

An ordinary brightener or additive can be added to the plating bath. For example, 0.1 to 20 g/l of a water-soluble brightener obtained by reacting phthalic anhydride with a reaction product of an aliphatic amine and an organic acid ester can be added to the bath.

When the plating bath of the present invention is used, an intended tin-zinc alloy coating having a thickness of, for example, 0.5 μm to 0.5 mm can be formed by the electroplating on a metal such as iron, nickel, copper or an alloy of them. Further, by varying the ratio of tin to zinc in the plating bath, various tin-zinc alloy coating compositions can be obtained. For example, a composition having a zinc content of 5 to 15 % by weight is used for the electric contact or the like; a composition having a zinc content of 15 to 45 % by weight is used when a high resistance to an aqueous salt solution and to corrosion is necessitated; and a composition having a zinc content of 45 to 90 % by weight is used for the formation of a coating having a high corrosion resistance which is to be exposed to air.

Although the electroplating conditions are not particularly limited, the plating bath temperature is preferably 10 to 70 °C, more preferably 10 to 40 °C and the current density is preferably 0.1 to 10 A/dm². The time period for the electroplating is not limited, but preferably 1 minutes to 2 hours, more preferably 5 minutes to 1 hour. In this connection, the substrate is a cathode and tin-zinc alloy is an anode. A weight ratio of tin to zinc in the anode is optional but preferably the ratio may be the same as in the alloy composition formed on the substrate.

The coating formed by using the electroplating bath of the present invention can be treated with a chromate by an ordinary method. The treatment with the chromate can be conducted by, for example, a method described in J.P. KOKOKU No. Sho 38-1110.

When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substrate having a complicated shape, and the chromate treatment becomes satisfactory. As a result, the effect of the coating film is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

The following Examples will further illustrate the present invention. The composition of the plating bath and the plating conditions can be changed depending on the object.

Example 1

The basic tin-zinc alloy plating bath used in the Examples of the present invention are given in Table 1.

Table 1 Basic plating bath used in Examples

Bath	Citrate bath	Gluconate bath	Pyrophos bath
<u>Bath composition</u>			
	Stannous sulfate	Stannous sulfate	Stannous pyrophosphate
	(40 g/l)	(40 g/l)	(20 g/l)
	Zinc sulfate	Zinc sulfate	Zinc pyrophosphate
	(40 g/l)	(40 g/l)	(40 g/l)
	Citric acid	Gluconic acid	Pyrophosphoric acid
	(100 g/l)	(120 g/l)	(100 g/l)
	Ammonium sulfate	Ammonium sulfate	
	(80 g/l)	(80 g/l)	
<u>pH adjustor</u>			
	Sodium hydroxide	Sodium hydroxide	Potassium hydroxide
	or ammonia water	or ammonia water	
Plating bath temp.: Citrate bath and gluconate bath: 25°C			
Pyrophosphate bath 60 °C			

In this Example, the electroplating was conducted at the above-mentioned bath temperature for 10 to 60 min, wherein an iron sheet was used as the cathode and a tin-zinc alloy sheet (weight ratio of tin to zinc is 50/50) was used as the anode and the current density was 0.2 to 5 A/dm².

The compositions of the tin-zinc alloy plating bath containing the amphoteric surfactant used in the Example and also of the coating alloy film obtained from the bath are given in Table 2.

For comparison, the compositions of the amphoteric surfactant-free plating bath and also of the coating alloy film obtained from the bath are also given in Table 2.

Table 2 Compositions of plating bath and formed coating alloy film

No.	Basic plating bath	pH of plating bath	Amphoteric surfactant	
			Compound	Amount
1	Citrate bath	6.0	Coconut oil alkyl-N-carboxyethyl-N-hydroxyethyl-imidazolium betaine chloride	5 g/l
2	Citrate bath	6.0	Coconut oil alkyl-N-carboxyethyl-N-hydroxyethyl-imidazolium betaine chloride	5 g/l
3	Citrate bath	9.0	Stearyldimethylammonium betaine	1 g/l
4	Citrate bath	5.0	Na salt of cetyldi(amino-ethyl)glycine	10 g/l
5	Citrate bath	5.0	Na salt of cetyldi(amino-ethyl)glycine	1 g/l
6	Citrate bath	6.0	Laurylamide propylbetaine	1 g/l
7	Citrate bath	6.0	Laurylamide propylbetaine	1 g/l
8	Citrate bath	6.0	Pentadecanoamide propylbetaine	10 g/l
9	Citrate bath	7.0	Sodium undecylaminoethyl-carboxylate	5 g/l
10	Citrate bath	7.0	Sodium undecylaminoethyl-	5 g/l

			carboxylate	
5	11	Gluconate bath	3.0	2-Myristyl-1-carboxymethyl-1-hydroxypropylimidazolinium betaine 2 g/l
10	12	Gluconate bath	6.0	2-Myristyl-1-carboxymethyl-1-hydroxypropylimidazolinium betaine 2 g/l
15	13	Pyrophosphate bath	9.0	Lauryldiethylaminoacetic acid betaine 5 g/l
20	14	Citrate bath	6.0	2-Cetyl-1-carboxymethyl-1-hydroxypropylimidazolinium betaine 1 g/l
	15	Citrate bath	7.5	Lauryldiethylammoniumbetaine 2 g/l
	16	Citrate bath	5.0	Lauryl-N-hydroxyethyl-N-sulfoethylimidazolinium betaine 5 g/l
25	31	Citrate bath	6.0	None -
	32	Citrate bath	9.0	None -
	33	Gluconate bath	3.0	None -
30	34	Gluconate bath	6.0	None -
	35	Pyrophosphate bath	9.0	None -
35	36	Citrate bath	6.0	None -
	32	Citrate bath	7.5	None -

Table 2 (continued)

No.	Other additives	Amount	Appearance of plated	Plating alloy composition (zinc content; %)
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				product	cathode current density		
					0.2A/cm ²	1.5A/cm ²	5A/cm ²
5	1	None	-	Dull	31.2	40.3	43.0
P2 →	2	Aromatic aldehyde	0.1 g/l	Semiglossy	28.0	38.6	39.2
-	3	None	-	Dull	25.5	38.8	41.2
10	4	None	-	Dull	20.7	35.6	34.7
	5	DIPSOL® DG-FR-7	0.1 g/l	Semiglossy	20.1	35.1	35.7
	6	None	-	Dull	21.3	38.4	39.4
15	7	DIPSOL® SZ-240S	8 ml/l	Semiglossy	20.5	35.1	38.5
	8	None	-	Dull	27.0	37.6	41.0
	9	None	-	Dull	21.5	34.9	37.7
20	10	DIPSOL® SZ-240S	8 ml/l	Semiglossy	19.3	34.4	38.2
P10 (v) →	11	Polyoxyethylene laurylamine (15 mol ethylene oxide adduct)	5 g/l	Semiglossy	20.5	35.9	39.3
25	12	None	-	Dull	23.3	36.6	39.0
	13	None	-	Semiglossy	25.0	38.9	40.5
30	14	Aliphatic amine/ organic acid ester/ phthalic anhydride reaction product	2 ml/l	Semiglossy	10.3	11.8	12.3
35	15	None	-	Dull	54.6	68.6	74.6
40 →	16	Epoxy compound/ propylene glycol reaction product	2 g/l	Semiglossy	67.9	80.3	82.4
45	31	DIPSOL® SZ-240S	8 ml/l	Semiglossy	12	35	37.5

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32	DIPSOL® SZ-240S	8 ml/l	Semiglossy	9.0	48.3	50.6
33	Polyoxyethylene laurylamine (15 mol ethylene oxide adduct)	5 g/l	Semiglossy	8.5	17.0	33.8
34	Polyoxyethylene laurylamine (15 mol ethylene oxide adduct)	5 g/l	Semiglossy	9	35	45
35	None	-	Spongy surface	-	-	-
36	Aliphatic amine/ organic acid ester/ phthalic anhydride/ reaction product	2 ml/l	Semiglossy	8.4	15.0	19.7
37	Polyethylene glycol	5 g/l	Semiglossy	18.1	40.2	51.9

In the above Table, Nos. 1 to 16 are Examples, and Nos. 31 to 37 are Comparative Examples. In Nos. 14, 15, 16, 36 and 37, the amounts of tin and zinc (g/l each in terms of the metal) in the bath were as follows:

No.	14	15	16	36	37
Tin	20	10	5	20	10
Zinc	1	20	20	1	20

Claims

1. A tin-zinc alloy electroplating bath which comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water.
2. A tin-zinc alloy electroplating bath as claimed in claim 1 wherein the amphoteric surfactant is imidazoline, betaine, alanine, glycine or an amide type amphoteric surfactant.
3. A tin-zinc alloy electroplating bath as claimed in claim 2 wherein the amphoteric surfactant is an imidazoline type amphoteric surfactant.
4. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims wherein the amphoteric surfactant is present in an amount of from 0.01 to 30 g/l.
5. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims wherein the water-soluble stannous salt is present in an amount of from 1 to 100 g/l in terms of metallic tin.
6. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims wherein the water-soluble zinc salt is present in an amount of from 0.2 to 80 g/l in terms of metallic zinc.
7. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims which is a cyanide-free bath.

8. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims which further comprises a carboxylic acid containing from 1 to 15 carbon atoms or pyrophosphoric acid.
- 5 9. A tin-zinc alloy electroplating bath as claimed in claim 8 wherein the carboxylic acid is present in an amount of from 40 to 400 g/l.
- 10 10. A tin-zinc alloy electroplating bath as claimed in claim 8 wherein the pyrophosphoric acid is in an amount of 30 to 300 g/l.
- 10 11. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims which has a pH of from 3 to 10.
12. A tin-zinc alloy electroplating bath as claimed in any one of the preceding claims which further comprises 0.1 to 20 g/l of a water soluble brightener.
- 15 13. A method for forming a tin-zinc alloy on a substrate by electroplating in a tin-zinc electroplating bath comprising an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and the balance of water wherein the substrate is a cathode and the tin-zinc alloy is an anode.
- 20 14. A method as claimed in claim 13 wherein the amphoteric surfactant is imidazoline, betaine, alanine, glycine or an amide type amphoteric surfactant.
- 15 15. A method as claimed in claim 13 or claim 14 wherein the amphoteric surfactant is present in an amount of from 0.01 to 30 g/l.
- 25 16. A method as claimed in any one of claims 13 to 15 wherein the water-soluble stannous salt is in present an amount of from 1 to 100 g/l in terms of metallic tin.
- 30 17. A method as claimed in any one of claims 13 to 15 wherein the water-soluble zinc salt is present in an amount of from 0.2 to 80 g/l in terms of metallic zinc.
18. A method as claimed in any one of claims 13 to 17 wherein the bath further comprises a carboxylic acid containing from 1 to 15 carbon atoms or pyrophosphoric acid.
- 35 19. A method as claimed in claim 18 wherein the carboxylic acid is present in an amount of from 40 to 400 g/l and pyrophosphoric acid is present in an amount of from 30 to 300 g/l.
- 40 20. A method as claimed in any one of claims 13 to 19 wherein the electroplating bath temperature is in the range of from 10 to 70 °C and the current density is in the range of from 0.1 to 10 A/dm².



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 0252

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	GALVANOTECHNIK vol. 82, no. 9 , September 1991 , GERMANY page 3046 'galvanische zinn-zink-überzüge als cadmiumersatz'		C25D3/60
A	FR-A-2 185 007 (SONY CORPORATION) * page 4, line 10 *		
A	SURFACE TREATMENT TECHNOLOGY ABSTRACTS vol. 29, no. 2 , March 1987 , GREAT-BRITAIN page 84 'electrolyte for electrodeposition of tin-zinc alloy coatings' & SU-A-1 294 878 (BOBROVSKII) 22 July 1985		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 April 1994	Examiner Nguyen The Nghiep, N
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	